Chemical Trends in Polymer NEXAFS: Carbonyl C 1s → $\pi^*_{C=O}$ transition

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Introduction: Near Edge X-ray Absorption Fine Structure (NEXAFS) spectra have excellent sensitivity for the chemical microanalysis of organic materials such as polymers. This chemical sensitivity is typically manifest in functional group sensitivity, where specific functional groups have unique spectroscopic fingerprints. In X-ray microscopy and microspectroscopy, these spectra can provide detailed chemical information of radiation sensitive organic materials at <100 nm spatial resolution. Chemical identification of "unknown" or unexpected microphases in nano-structured polymer materials observed by X-ray microscopy can be obtained if the chemical sensitivity of the NEXAFS spectra is adequately understood.

Here we demonstrate an analytically useful trend in the characteristic "fingerprint" of the carbonyl group, the C 1s (C=O) → $\pi^*_{C=O}$ transition, as a function of changes in the immediate chemical environment.

Methods and Materials: NEXAFS spectra were acquired in transmission using the SUNY-SB STXM microscope on the X1A beamline. Thin films were prepared by ultramicrotomy or spin casting. X-ray microscopy was essential for identifying uniform thin regions (~100 nm thick, ~10 micron diameter, without pin holes) for accurate transmission spectroscopy. Spectra were calibrated to the C 1s → Rydberg transitions of CO_2 which was leaked into the microscope's He purge. Several spectra in **Figure 1** have been presented previously (**B**, **C** [UA&99]) or were reacquired at higher resolution for this study (**G** [UH&97]).

Results: **Figure 1** presents the C 1s NEXAFS spectra for a range of model polymers with the carbonyl group in different functional group environments, from ketone (**H**) to carbonate (**A**). A clear trend in the C 1s(C=O) → $\pi^*_{C=O}$ transition with the local bonding environment of the carbonyl group is observed. The energy of this transition varies with the identity of the atoms bonded to the carbonyl carbon atom (i.e. X_1-C(O)-X_2): highest for $X_{1,2}$ = Oxygen, lowest for $X_{1,2}$ = Carbon, with $X_{1,2}$ = Nitrogen intermediate (i.e. O > N > C). The dominant cause of these shifts is the inductive effect of the neighboring atoms on the carbonyl carbon 1s binding energy. The origin of these shifts, explored by *ab initio* calculations [UAS00], is mostly but not entirely due to binding energy shifts.

Conclusions: C 1S NEXAFS spectra are remarkably sensitive to the local chemical environment of the carbonyl group. Characterization of these chemical shifts and related chemical effects is required for harnessing the analytical potential of these distinctive NEXAFS transitions for qualitative chemical microanalysis of organic materials by NEXAFS microscopy and micro-spectroscopy.

References: UA&99 Urquhart, S.G.; Ade, H.W.; Smith, A.P.; Hitchcock, A.P.; Rightor, E.G.; Lidy, W.*J. Phys. Chem. B* 1999, *103*, 4603-4610.; UH&97 Urquhart, S.G.; Hitchcock, A.P.; Smith, A.P.; Ade, H.; Rightor, E.G. *J. Phys. Chem. B* 1997, *101*, 2267-2276.; UAS00 Urquhart, S.G., Ade, H., Stöhr, J. manuscript in preparation, 2000.

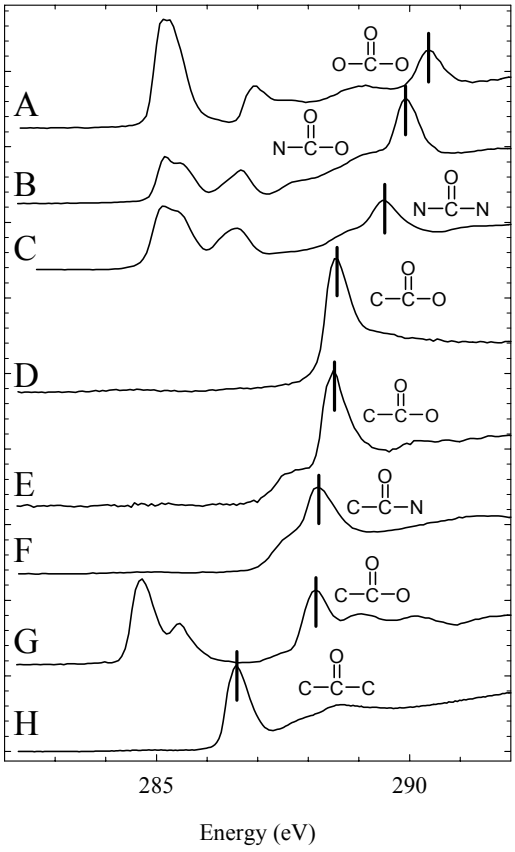

Figure 1. C 1s NEXAFS spectra of model polymers: (**A**) poly(carbonate), (**B**) polyurethane, (**C**) polyurea, (**D**) poly(ethylene succinate), (**E**) poly(methyl methacrylate), (**F**) nylon-6, (**G**) poly(ethylene terephthalate, and (**H**) poly(vinyl methyl ketone). The C 1s(C=O) → $\pi^*_{C=O}$ transition for each polymer is indicated by the line. The motif for the local bonding environment about each carbonyl group (X_1-C(O)-X_2) is indicated.